**Title:** The Reaction Specificity of Nanoparticles in Solution: Application to the Reaction of Nanoparticulate Iron and Iron-Bimetallic Compounds with Chlorinated Hydrocarbons and Oxyanions

**Project Number:** 44076/42184 (project jointly funded by EMSL and BES Chemistry)

**Name of Laboratory:** Pacific Northwest National Laboratory with collaborators from the Oregon Health and Sciences University and the University of Minnesota

**Problem Statement and Research Objective:**

The prospect for better remediation technologies using nanoparticles of iron, iron oxides, and iron with catalytic metals (i.e., "bimetallics) has potentially transformative implications for environmental management of DOE sites across the country. Of particular interest is the potential to avoid undesirable products from the degradation of chlorinated solvents by taking advantage of the potential selectivity of nanoparticles to produce environmentally benign products from $CCl_4$. Chlorinated solvents are the most frequently reported subsurface contaminants across the whole DOE complex, and carbon tetrachloride ($CCl_4$) is the chlorinated solvent that is of greatest concern at Hanford (U. S. Department Energy 2001). In evaluating technologies that might be used at the site, a critical concern will be that $CCl_4$ reduction usually occurs predominantly by hydrogenolysis to chloroform ($CHCl_3$) and methylene chloride ($CH_2Cl_2$), both of which are nearly as problematic as $CCl_4$ (National Research Council, 1978). Competing reaction pathways produce the more desirable products carbon monoxide (CO) and/or formate ($HCOO^-$), and possibly $CO_2$, but the proportion of reaction that occurs by these pathways is highly variable. Iron-based metallic and oxide nanoparticles have been shown to have enhanced reactivity towards a variety of chemical species, including chlorinated hydrocarbons and reducible oxyanions. Possibly of greater importance is the ability of nanoparticles to select for specific reaction products, potentially facilitating the formation of more environmentally acceptable products. The purpose of this study is to develop a fundamental understanding of the mechanism responsible for the overall particle reactivity and reaction selectivity of reactive metal and oxide nanoparticles. To achieve this objective the project involves the synthesis (using solution and vacuum synthesis methods) and characterization of well-defined nanoparticles, measurements of particle reactivity in solution or vacuum environments, and theory and modeling efforts to rationalize particle structure and reactivity.

**Research Progress and Implications:**

*Synthesis and Characterization of Nanoparticles*

We have produced and characterized the nature of three qualitatively different types of nanoparticles produced by different methods. These particles provide the basis of solution reactivity studies described below. A vacuum based process produces uniform sized metal core particles with an iron-oxide coating. A solution based reduction process forms small grained metal rich nanoparticles with a borate rich oxide coating. An oxide reduction process produces irregularly shaped nanoparticles, many of which have a metal core and iron oxide shell. We have used transmission electron microscopy (TEM) to get a measure of particle size, shell thickness and particle structure; x-ray photoelectron spectroscopy (XPS) to examine the composition of the particles surfaces (coatings) and to get a measure of surface contamination; x-ray diffraction (XRD) to get a measure of particle structures and to obtain a measure of crystallite size; X-ray absorption spectroscopy (XAS) including scanning transmission x-ray microscopy (STXM) as an

additional measure of particle composition and to confirm the mixture of oxide and metal compositions; and BET for surface area determination.

A significant, but not unexpected, result of characterization of particles that we have produced and have been produced by others is that there wide variations in the coating thickness, surface chemistry, contamination, shape and sizes of nanoparticles produced by different methods and stored for different times [Baer et. al. 2005]. There is also a diagenesis or transformation of the nature of the particles that takes place as the particles are stored or exposed to various reactants. A significant challenge in understanding, predicting and controlling the overall reactivity and lifetime of these particles depends upon knowledge of the history and detailed processing conditions of the materials.

*Reactivity Measurements*

Solution reactivity studies to date have provided two significant results: First, the overall reactivity of nanoparticles in aqueous solution is primarily determined by the surface area and is not anomalously increased due to small particle size; Second, the nature of the surface coating on a nanoparticle can make a factor of four or more difference in the production of toxic versus non-toxic products during reduction of carbon tetrachloride.

We have found no evidence to support the common assertion that nanoparticles are intrinsically more reactive than colloidal particles, under the conditions of experiments that we had performed [Nurmi et al. 2005]. Since this conclusion has fundamental and practical implications, we've given some priority to determining if it holds over a wider range of conditions. We've done this by measuring the kinetics of $CCl_4$ degradation with a wider range of nano $Fe^0$ preparations, over a wider range of experimental conditions, and compiling all relevant data that has been reported previously. The results, which are summarized in Figure 1, clearly show that while nano $Fe^0$ is more reactive on a mass basis (because it's specific surface area is high) the surface area

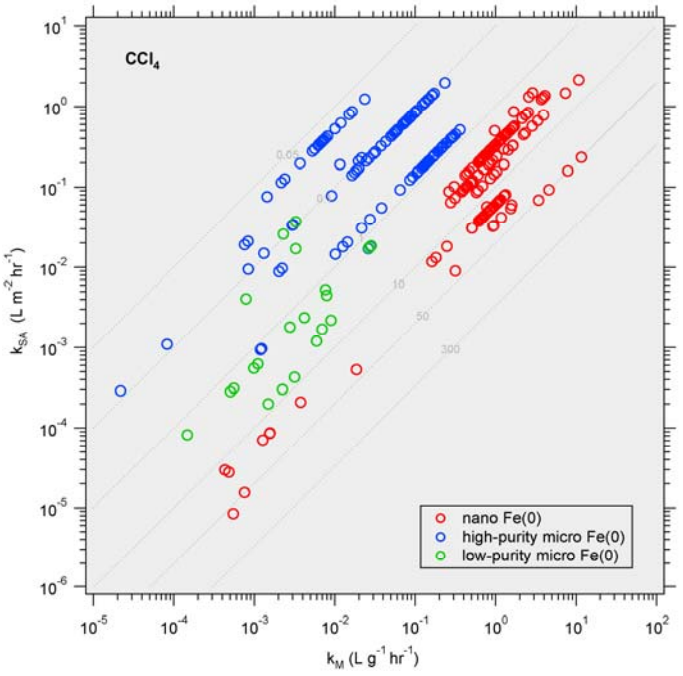


Figure 1. Summary plot of surface area normalized reaction rates versus mass normalized reaction rates for reduction of $CCl_4$. On a mass basis nanoparticles are highly reactive, but they are usually equivalent to other particles when adjusted for surface area. Most of the data shown for nano $Fe^0$ are from Nurmi et al. (2005) or are to be published in Sarathy et al. The data for micro $Fe^0$ are mostly from previously published work by Tratnyek et al. There is a spread due to the different types and preparations methods for the particles as well as different solution conditions. .

normalized rate constants approach a limit of about 1 L $m^{-2}$ $hr^{-1}$ regardless what type of $Fe^0$ is used or what experimental conditions are used. This result implies a fundamental limit to the effects of nanoparticle reaction rates when applied in aqueous media (contaminant degradation can only be so fast).

A second major conclusion is that the structure and chemistry of the core-shell metal nanoparticles can significantly alter the reaction pathway. Our work [Nurmi at al. 2005] demonstrated that nanoparticles produced by the hydrogen reduction process had a significantly decreased production of chloroform in comparison to micron sized iron particles or nanoparticles formed in solution by a borohydride reduction process. Follow on Electron Paramagnetic Resonance (EPR) measurements on the hydrogen reduced material indicate that the relative rates of electron transfer and hydrogen transfer processes associated with reduction of contaminants such as $CCl_4$ vary as a function of the time the particles have been in water. This change in reaction process will likely alter the reaction pathways as a function of particle time in solution and is subject to current experiments. An objective is to understand and control nanoparticle properties to optimize the favorable reaction pathways.

*Theory and model systems*

Properties of the oxide shells surrounding metallic iron nanoparticles in solution have a significant influence on the chemical properties of the particles. For controlling reaction pathways, two of the most important characteristic of the shells involve the trapping and mobility of charge near the surface and how contaminant molecules interact with the shell surface. A new self-consistent self-interaction-corrected density functional theory has been developed and is being applied to the understand charge transport and electron surface trapping in oxide shells [Bylaska, Tsemekhman, and Gao 2005]. With this new computational "tool" in hand we are uniquely poised to quantify reliably the differences in redox potentials between bulk and surface cationic sites on the oxide surfaces. Since charge transport and mobility help define reaction pathways, this information is critical to the control of reaction branching.

Details of the interactions of chlorinated hydrocarbon molecules with supported oxide films and nanoparticles have been experimentally measured using surface chemical methods. The current work has focused on interactions of $CH_4$ and its chlorinated derivatives and water with model FeO materials. Each of these molecules interacts weakly with this surface consistent with a non-specific reduction site for contaminant reduction on these surfaces.

**Planned Activities**

A renewal proposal for this program is currently under review. Based on our current understanding of the critical importance of the shell properties of reactive metal nanoparticles, the focus of the renewal proposal is to understand the properties of the nanoparticle shells that alter the competing reactions on the surfaces and to design particles to optimize the desired reaction pathways and time evolution of the particles. Experimental and theoretical studies related to electron transfer, hydrogen availability and molecule-shell interactions have been proposed.

## Information Access – FY05 Publications supported by this program


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